Process for applying a layer of an electrically conductive material to another electrically conductive material.

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Abstract of **EP 0217081 (A1)**

1. A process for applying a layer of an electrically conductive material on top of another electrically conductive material by electrochemical deposition, wherein a vessel which is provided with an orifice and contains an electrode and a solution from which an electrically conductive material is formed by electrochemical deposition is passed over the surface of the other electrically conductive material, so that in the region of the orifice the solution comes into contact with the surface of the other electrically conductive material, the other electrically conductive material is connected to the counterelectrode and the electrically conductive material is deposited electrochemically from the solution on the surface of the other material.

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Method for applying a layer from an electrical conductive material on another electrical conductive material

The invention relates to a method for applying a layer from an electrical conductive material on the surface of another electrical conductive material, with which one applies a solution, from which by electrochemical deposition another electrical conductive material, applies the solution develops on the surface of the other material and separates the electrical conductive material on the surface of the other material.

After the prior art methods of the galvanotechnics e.g. the Galvanostegie (electroplating) from electrolyte solutions, the metal salts contain coats on subject-matters cathodic deposited. So one can e.g. Metal coatings on the surfaces of other metals or the same metal apply. In addition, it is possible, metal coatings on not conductive materials, whose surface is conductive equipped to separate. Such methods e.g. become. in Römpps "chemistry lexicon" Frank' publishing house action Stuttgart, the bottom references galvanotechnics and Galvanostegie, described. A very detailed representation of the known methods of the galvanotechnics is in Ullmanns Encyklopädie of the technical chemistry, 4. Edition, belt 12, side 137 to side 200.

The electrochemical deposition of electrical conductive polypyrrole on metals is known (see. among other things US-PS 3,574,072 and DE-A-30 49,551). Here pyrrole becomes and/or. the pyrrole/Comonomer mixtures in electrolytic solution means in presence of Leitsalzen electrically zed, organic in all rule, whereby by anodic oxidation form for Pyrrol polymers and separate at the anode. The Leitsalze, for example the alkali metal, ammonium or Phosphonium salts with anions from the group BF4< -> , AsF6< -> , SbF6< -> , PF6< -> , SbCl6< -> , ClO4< -> , HSO4< -> or SO4< 2>< -> here at least partly become, in Pyrrol polymers - likely in complex bound form - incorporated and lend an high electrical conductivity up to approximately 10 2 ohms to the so< prepared> Pyrrol polymers< ->¹ cm< ->¹.

After an older proposal of the patent application P 35 08 266,6 one can achieve a particularly intense connection between metal and conductive polymers by it that one connects the surface of the metal with metal complexing agents treated and then a solution, which contains and a Leitsalz of anodic oxidizable monomer with a cathode, the metal surface than anode switches and monomers to these waiters flat polymerized. Thereby e.g. Is it. possible, composites from conductive polymers and unedlen metals, e.g. Aluminium to manufacture like one it as electrodes in electrical memory elements required.

Object of the invention is a method for applying a layer of an electrical conductive material by electrochemical deposition on another electrical conductive material.

Object of the invention becomes by methods dissolved, with which one a container, which is provided with an opening and an electrode and a solution contains, from whom from electrochemical deposition an electrical conductive material, results, across the surface of the other electrical conductive material leads, so that the solution comes in the range of the opening of the container with the surface of the other electrical conductive material into contact, which connects other material with the counter electrode and electrochemical on the surface of the other material separates electrical conductive material from the solution.

The method of the invention allowed it, e.g. a metal layer on the surfaces of the electrical conductive material only at the locations to apply, which contains the anode as well as a metallic salt solution with the opening of the container that, into contact comes. By moulding of the opening one can apply layers in arbitrary width on the desired locations of the surface of the material. By corresponding guide of the contained container over the surface arbitrary patterns of the coating on the desired locations know the anode, e.g. in the form of signatures, on the material surface applied become.

The method of the invention allowed it in addition, to apply an electrically conductive layer polymers on the surfaces of a metal only at the locations which contains the cathode as well as a solution of monomers with the opening of the container that, into contact comes. The metal is connected as anode, so that that becomes monomers electrochemical polymerized and separates on the metal surface. Also here the cathode can know of the contained container over the metal surface arbitrary patterns of the coating on the desired locations, e.g. by corresponding guide. in the form of signatures, on the metal surface applied become.

To the practice of the method used one a container, which is provided with an opening and is in that an electrode incorporated. The container contains in addition a solution from by electrochemical starting from divorce a layer of the electrical conductive material on the other material develops. The container becomes so disposed that the opening becomes guided over the surface of the other material. It becomes thereby a distance from surface to the opening selected, that it allowed that the solution the surface wetted, i.e. thus with the surface into contact comes. It can be convenient to arrange in the opening an open celled foam or a nonwoven fabric which works as Schreibdocht, so that the solution uniform on the surface of the other material with the transportation of the fleece over the surface wetted. For applying signatures on surfaces can e.g. the container in form of a stylus formed its, so that by corresponding guide of the pin over the surface signatures can be trained.

The materials, becomes applied on which the one layer of an electrical conductive material, can be non-metallic metallic or, provided that they are electrical conductive. The method is suitable in particular for applying metal layers on other metallic materials, like it usually in the technology use finds, e.g. Steel, nickel, nickel alloys, aluminium, duralumin, titanium, magnesium.

The non-metallic materials, which are electrical conductive equipped, can e.g. Plastics its, which are for the effectuation of the conductivity metal powders or soot added. In addition, it is possible to equip the surface of the plastics after the methods of the electroplating conductive. In addition as non-metallic materials so called conductive plastics come such as polypyrrole, polyacetylene or Polyphenylen into question. In addition metallic foils are e.g. suitable. by vaporizing with metal conductive made became.

After a particular embodiment of the method one can apply layers of conductive polymers on the surfaces of metals. With these methods the container contains a cathode and a solution one by anodic polymerization polymerizable monomers as well as a Leitsalzes. The surface of the metal is connected as anode.

When monomers, which form electrical conductive polymers, such compounds become used, which anodic oxidized to become to be able. One can use thus for example alkynes or aniline as monomers, so that itself Polyalkine and/or. Polyanilin as layer on the metal surface forms. Monomers can selected be from the class of the five-membered heterocyclic compounds, which nitrogen or sulphur as heteroatom and in addition a pi - electron system is more conjugated fertilizes contained. Examples of these compounds are such from the class of the pyrroles and that Thiophene. From the pyrroles are e.g. suitable. the unsubstituted pyrrole in addition, N-substituted pyrroles such as N-Alkylpyrrol. Other substituted pyrroles can find in addition, such as 3,4-Dialkylpyrrole or 3,4-Dichlorpyrrole use. From the compounds of the class that Thiophene is suitable in particular the unsubstituted Thiophen as well as 2 - or 3-Alkylthiophene, e.g. 2,3-Diethylthiophen. In addition, these five-membered heterocyclic compounds mentioned can together with other copolymerizable compounds, like e.g. Furanen, thiazole, oxazole or imidazole or aniline and derivatives, polymerized become. Prefered ones as monomers are however pyrrole or Thiophen

The polymerization of this monomers made in presence of Leitsalzen, which become also referred as complexing agents or dopants. As Leitsalze have themselves e.g. KHSO4, Na2SO4, HCOOH, LiClO4, HClO4, NEt4ClO4, NBu4ClO4, KAlF3, NaAlF6, KBF4, K2ZrF6, K2NiF4, HO2 (NO3) 2, H2SO4, FeCl3, NOPF6, KAsF6 or NaPF6 preserved. The concentration of the Leitsalze is so sized that on 3 mol used monomers or the mixtures that monomers at least 1 mol of the listed above Leitsalze used become. Sulfonic acids of the pyrrole or the Thiophens can become both and monomers and and Leitsalze used. Suitable ones are

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also anions of aromatics with acidic groups, e.g. substituted aromatic sulfonic acids or polysulfone-acidic. The guidance salt concentration is with the method generally between 0,001 to 1, preferably 0.01 to 0.1 Mol/l solvents.

The concentration monomers in the solvent amounts to here generally approximately around 0,1 mol per liter solvent. In addition, it can within wide limits fallen below and/or. are exceeded. Convenient ones one works with concentrations from 0,01 to 1 mol monomer per liter solvent.

As electrolytic solution means particularly suitable is the polar organic solvents conventional for the anodic oxidation of the heterocyclic compounds specified above, which are able to loosen monomers and the Leitsalz. The solvent should be as aprotic ones as possible. Prefered ones are alcohols, ethers, like 1,2-Dimethoxyethan, Dioxantetrahydrofuran, acetone, acetonitrile, dimethylformamide or propylene carbonate.

The other material coated with conductive polymers becomes connected thereby than anode. The cathode can e.g. of another metal such as platinum, molybdenum, tungsten or of stainless steel, nickels or titania consist.

The vessel, which contains the cathode, provided with opening, is convenient prepared from a non conductive cloth. Suitable ones e.g. are: Plastics such as polytetrafluoroethylene, polypropylene, polyethylene. In addition the vessel is provided with an opening, which is connected with the environment area, so that the electrolyte solution, which contains monomers, from which over the surface other material led opening withdraw can. The opening, which is course-turned the surface, becomes so formed that one receives the desired width of the layer which can be applied. The vessel becomes now in such a manner guided that the opening only the locations of the surface touched, over the surface, is desired at which a layer.

The reaction temperature with that the method operated proved, as uncritically, so that in a wide range can be worked, so long the solidification temperature and/or. the boiling temperature of the electrolytic solution means not under and/or. one exceeds. Generally as reaction temperature a range from -20 to +40 DEG C as favourable proved, whereby one normally works at room temperature (22 to 24 DEG C). In all other respects the known electrolysis conditions known for methods for anodic oxidizing that monomers can be kept. Convenient one lies the voltage, becomes operated in which the electrochemical polymerization, within the range of 1 to 150 volts, preferably within the range of 2 to 20 volts. For the current density have themselves values from 0,5 to 100 mA/cm< 2>, preferably from 0,1 to 3.5 mA/cm< 2>, when proved favourably. Generally one aims at thickness of the applied layer of conductive polymers between 10 and 100 mu m. The obtained coated metals become subsequent solvents with solvents washed and dried, adherent to the removal. In prepared the according to invention composites that is present polymers as complex cation polymers with the Gegenanion of the Leitsalzes. The electric conductivity polymers lies usually within the range of 10 to 10< 2> S/cm.

After another particular embodiment of the method the container of the one anode and a metallic salt solution become contain guided over the surface of another electrical conductive material, which becomes material as cathode connected and the metal from the solution cathodic deposited.

The electrolyte solution, from which the metals become cathodic deposited, can in principle everyone of the cathodic separatable metals contain. Preferably the solutions contain salts of metals, which result in resistant coats on the surfaces of the materials. In addition, possible metals oxidizable at the air are to be separated. If concern is supported for the fact that the metal layer does not come with the oxygen of the air into contact. Such metals can e.g. Alkali metals or alkaline earth metals its, if it as coats on plastics e.g. on electrical conductive polymers applied e.g. become. find use as electrodes. The metal salts are in an electrolytic solution means dissolved. Here preferably Dioxan or tetrahydrofuranes come into Frage. Es are suitable in addition, high-boiling organic solvents, as polyethylene oxide and/or polypropylene oxide, which are terminal etherified with methyl groups.

Mixtures from water and with water mixable organic solvents, which solve the metal salts, are particularly favourable. The metallic salt solutions contain favourably between 0,01 and 3 mol/l the metal salt.

In the container, in which the metallic salt solution is contained, in addition an anode disposed is, those with the solution in compound stands and/or. from the solution wetted becomes. The anode can e.g. of a metal such as platinum, molybdenum, tungsten or of stainless steel, nickels or titania consist. The vessel, which contains the anode, provided with opening, is prepared like mentioned above, from a non conductive cloth. The electrolyte solution, which contains the metal salt, withdraws from the opening led across the metal surface. The opening, which is course-turned the material surface, becomes so formed that one receives the desired width of the layer which can be applied. The vessel becomes now in such a manner guided that the opening only the locations of the surface touched, over the material surface, is desired at which a metal layer.

The other operations to the practice of the method do not differ from the methods of the galvanotechnics. They are in the indicated above literature places described and the skilled person known.

The temperature with that the method operated proved, as uncritically, so that in a wide range can be worked, so long the solidification temperature and/or. the boiling temperature of the electrolytic solution means not under and/or. one exceeds. Generally as reaction temperature a range from +5 to +40 DEG C as favourable proved, whereby one normally works at room temperature (22 to 24 DEG C). In all other respects the known electrolysis conditions known for methods to the cathodic deposition of metals can be kept. Convenient one lies the voltage, becomes operated in which the electrochemical deposition, within the range of 1 to 150 volts, preferably within the range of 2 to 20 volts. For the current density have themselves values from 0,5 to 100 mA/cm< 2>, preferably from 0,1 to 3.5 mA/cm< 2>, when proved favourably. Generally one aims at thickness of the applied metal layer on the conductive material between 0,1 and 100 mu m, preferably between 1 and 10 mu m. The obtained coated materials become subsequent solvents washed and dried adherent to the removal.

Example 1

An automobile body from steel becomes connected as anode. Predetermined locations of the surface of the body now a container in the distance is led past of 0,5 cm, which contains the electrolyte solution and of monomers. The opening has a circular diameter of approximately 1 cm. It became a current density of 20 mAmp/cm< 2> between the surface of the anode and the cathode kept. The vessel was with a solution of 0,01 Gew,% pyrrole and 0.01 Gew,% of the tetrabutylammonium salt of the Phenylsulfonsäure in acetonitrile filled. The opening of the vessel is with an open celled polyethylene foam filled, that the electrolyte solution, which contains monomers, wetted, so that the wetting of the metal surface over this polyethylene foam made. The movable cathode vessel becomes now guided over the surface of the body. Provided itself a polymerization time per cm< 2> of in each case 0.5 minutes. The container became continuous guided in straight direction, so that itself a strip of 1 cm has width from polypyrrole and 1.20 cm length on the surface of the body formed. The strip conductive polymers had a thickness of 15 mu. The polymer clings to solid on the surface.

Example 2

One works as in example 1, however as electrolyte a mixture from acetonitrile with 10% water used. As Leitsalz the Tributylammoniumsalz of the Kupferphthalocyanintrisulfonsäure serves. Thereby a special solid adhesion of the Polypyrrolschicht on the metal surface becomes achieved.

In same way the Tributylammoniumsalz of the Anthrachinonsulfonsäure can become used as Leitsalz.

Example 3

One works as in example 1, however as electrolyte propylene carbonate with Tetrabutylammoniumperchlorat as Leitsalz used.

Example 4

One works as in example 1, however as electrolyte methylene chloride with Tributylammoniumtolylsulfonat as Leitsalz used; additional contains the electrolyte, related to the methylene chloride 2 Gew,% polyether sulfone.

Example 5

As in example 1, however tetrahydrofurane with Fe (ClO4) becomes as Leitsalz used as electrolyte; additional contains the electrolyte, related to the tetrahydrofurane 1.5 Gew,% polyvinyl chloride; as monomer serves 3-Methylthiophen.

Example 6

A steel housing becomes connected as cathode. Predetermined locations of the surface of the steel housing a container in the distance is led past by 0,5 cms, the metallic salt solution and the anode contains. The opening has a circular diameter of approximately 1 cm. It became a current density of 2 mA/cm< 2> between the surface of the housing and the anode in the container, connected as cathode, kept. The vessel was filled with a solution of a mixture from water and polypropylene glycol in the ratio 1:1, which contains 0.01 Gew,% silver nitrate and 0.1 Gew,% of the tetrabutylammonium salt of the Phenylsulfonsaure. The opening of the vessel is filled, which lets through the electrolyte solution, with an open celled polyethylene foam, which contains the metal salt, so that the surface of the metal case becomes wetted. The movable vessel, which contains the anode, becomes now guided over the surface of the steel housing. A

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disconnection time per cm 2< places itself> of in each case 0.5 min. . The container became continuous guided in straight direction, so that itself a strip of 0,2 cms has width from silver and 1,2 cms length on the surface of the housing formed. The strip of the deposited silver has a thickness of 1,5 mu. It clings to solid on the surface of the steel housing.

One works as in example 6, however an housing from the conductive Kunststoffpolypyrrol used. The electrolyte is a mixture from acetonitrile with 10% water. The solution contains the Tributylammoniumsalz of the Kupferphthalocyanintrisulfonsäure as Leitsalz. Thereby a special adhesion of the metal on the Polypyrrolschicht achieved becomes. In addition the solution contained Kobaltnitrat, whereby the concentration of the Leitsalzes and the metal salt, to which in the example 6 indicated correspond. It becomes a solid cobalt layer on the polypyrrole obtained.

It can be worked also in the same way without Leitsalz.

Example 7

One works as in example 6, however as electrolyte propylene carbonate and as metal salt nickel ii-perchlorate used.

In same way one can use an aqueous polyvinyl alcohol solution and tin ii-chloride as electrolyte as metal salt.

Becomes thus adherent nickel and/or. Tin layers on the steel surface obtained.

Example 8

One works as in example 7, however bottom argon inert gases. The electrolyte contains tetrahydrofuranes and Kaliumperchlorat as metal salt. It becomes an adherent layer of potassium on Polylpyrrol obtained.

In same way a thermoplastic resin can become used at location of polypyrrole, whose surface is conductive equipped.

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Result Page

1. Method to applying a layer of an electrical conductive material by electrochemical deposition on another electrical conductive material, characterised in that one a container, which is provided with an opening and which contains an electrode and a solution from the conductive material electrical by electrochemical deposition develops, across the surface of the other electrical conductive material leads, so that the solution comes in the range of the opening with the surface of the other electrical conductive material into contact, which connects other electrical conductive material with the counter electrode and which electrical conductive material from the solution electrochemical on the surface of the other material separates.

2. Process according to claim 1, characterised in that one a container, which contains a cathode and a solution one by anodic polymerization polymerizable monomers as well as a Leitsalzes across the surface of a Metalles leads, the metal as anode switches and monomers the anodic polymerized.

3. Process according to claim 2, characterised in that one as monomers compounds from the class of the pyrroles or Thiophene used.

4. Process according to claim 1, characterised in that one a container, which contains an anode and a metallic salt solution, across the surface of an electrical conductive material leads, the material as cathode switches and the metal cathodic separates.

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